SUPPRESSION OF CUP-BURNER DIFFUSION FLAMES BY SUPER-EFFECTIVE CHEMICAL INHIBITORS AND INERT COMPOUNDS[*]

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INTRODUCTION

The burning velocity and extinction strain rate reduction caused by addition of the iron compounds $Fe(CO)_5$ and ferrocene (($C_5H_5)_2Fe$, Fec) to premixed Bunsen-type and counterflow diffusion flames has been observed [1-4]. Recent work has extended the work in premixed flames to the new agents, tetramethyltin (TMT, $Sn(CH_3)_4$) and methylcyclopentadienylmanganese tricarbonyl (MMT, $C_9H_7MnO_3$) [5], both of which are more effective than CF_3Br, but less so than $Fe(CO)_5$. No tests with these agents, however, have been done in flames resembling fires. The present work remedies this deficiency by presenting results for addition of these highly effective agents to cup-burner flames. Not only do cup burners have flame structures that are a reasonable approximation to those in fires, but they are also widely used by the fire protection industry as a metric to assess fire suppressant performance. Hence, measurements of agent performance in cup burners have clear relevance to their eventual use.

BACKGROUND

It is well known that some metallic compounds reduce the burning velocity of premixed flames one or two orders of magnitude more than does CF_3Br. Previous work has shown this superior performance for iron pentacarbonyl $Fe(CO)_5$, tetraethyllead $(C_2H_5)_4Pb$, chromyl chloride CrO_2Cl_2, and ferrocene $(C_5H_5)_2Fe$. The overall reaction rate, which is related to the square of the burning velocity [6], is thus greatly reduced by these agents under premixed conditions. If means could be found to incorporate such agents in a practical fire suppressant (particularly for unoccupied spaces), very effective agents may be possible.

One of these agents, $Fe(CO)_5$, has recently been studied in some detail. Experiments and modeling have quantified its performance and explained its mechanism of inhibition for a variety of conditions [3, 7-9]. The strong inhibition is believed to occur from a catalytic radical recombination cycle involving iron oxides and hydroxides: $FeOH + H \leftrightarrow FeO + H_2$; $FeO + H_2O \leftrightarrow Fe(OH)_2$; and $Fe(OH)_2 + H \leftrightarrow FeOH + H_2O$, which yields the net reaction: $H + H \leftrightarrow H_2$. This mechanism leads to very strong inhibition for $Fe(CO)_5$ mole fractions below about 100 ppm[†]; however, above this value,

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[†] All reference to ppm in the present paper are on a volume or molar basis, and refer to µL/L.

the inhibitor begins to lose its effectiveness. This is believed to occur from condensation of the active iron-containing intermediates to particles [10]. The reduction in the effectiveness of $Fe(CO)_5$ as the mole fraction increases was shown to be much more dramatic in premixed flames than in counterflow diffusion flames. Any practical fire suppressant using these super-effective agents would require some method to overcome the loss of effectiveness and the high toxicity.

One approach to overcoming the loss of effectiveness is to combine catalytic agents with inert agents. In this case, the overall reaction rate is lowered in part through radical recombination by the catalytic agent, and in part through the lower temperature from the added diluent.   This approach has been discussed in work since the 1950's [9, 11-15], which suggested that combinations of thermally acting and catalytic agents might prove beneficial. These predictions have been confirmed in premixed flames with ferrocene and CO_2 as the inhibitors [4] and in premixed and counterflow diffusion flames inhibited by $Fe(CO)_5$ at reduced oxygen mole fraction in the oxidizer (which is equivalent to adding diluent nitrogen) [3]. Moreover, previous tests with $Fe(CO)_5$ at reduced oxygen mole fraction, and tests with ferrocene blended with CO_2, show that addition of an inert compound can actually enhance the performance of the catalytic agent.   Nonetheless, it is generally not known a priori if the combination of an inert with the catalytic agents will be effective in a particular flame configuration: the lower oxygen mole fraction (or added diluent) makes the catalytic effect stronger, while the lower temperature (and consequently longer residence in premixed flames) increases the likelihood of condensation [10].

Motivated by these results, tests of ferrocene together with an inert compound generated by a solid propellant gas generator (SPGG) have recently been conducted in an enclosure containing a spray flame [16]. Unfortunately, the combination did not have the intended high efficiency, and failed to extinguish the flame. As described above, the combination of inert and catalytic agents has been shown to be effective in premixed flames and counterflow diffusion flames. Not withstanding, carefully controlled tests like those in the premixed and counterflow diffusion flames have not been performed in cup-burner flames. In order to explore possible reasons for the lack of effectiveness of Fec with the SPGG in suppressing the spray flame tested, we performed tests with catalytic metal-based inhibitors and CO_2 added to the air stream in a cup burner.

Based on our recently acquired understanding of the action of iron in flames, addition of $Fe(CO)_5$ *alone* to the air stream of a cup burner would not be expected to be efficient at extinguishing the flame. This is because particle formation acts as a sink for the active gas-phase inhibiting species, keeping the maximum inhibiting species mole fractions at their saturation value. That is, adding more and more $Fe(CO)_5$ to the air stream does not increase the gas-phase mole fraction of active inhibiting species; the eventual extinction would likely come about through the much less efficient processes

involving the condensed-phase particles (including surface radical recombination, the particle heat capacity, and particle radiation heat losses). However, based on the premixed results with Fec and CO_2, we would expect that added Fec (or $Fe(CO)_5$) should significantly *reduce* the amount of CO_2 necessary to extinguish the cup-burner flame. This approach should be effective for two reasons. First, based on premixed flame results presented previously, we expect that adding 100 ppm or above of iron should reduce the overall reaction rate by about a factor of four (i.e. about a factor of two reduction in flame speed); and second, with added inert the effectiveness of the iron in the gas phase should be improved. Hence, we would expect that first adding an effective catalytic agent to the air stream would reduce the amount of CO_2 required to extinguish the flame.

Two approaches are used in the present work. In the first, catalytic agents ($Fe(CO)_5$, TMT, MMT, Br_2 , and CF_3Br) are added to the co-flowing air stream at various volume fractions, and the amount of added CO_2 required to extinguish the flame is determined. This is the typical cup-burner flame extinction test. In the second approach, the flame is extinguished in the same manner, but at each inhibitor volume fraction up to extinction, the fuel consumption rate of the burner is measured. The fuel consumption rate (which is determined by the heat feedback from the flame) scales approximately linearly with total heat release. Typically, the fuel consumption rate decreases as inhibitor is added to the air stream, and at extinction, the fuel consumption rate approaches zero. In the present tests we measure the fuel consumption rate in the presence of increasing amounts of CO_2, with and without added catalytic inhibitor in the air stream. An effective fire suppressant would be expected to reduce the fuel consumption rate, much as do fire retardants added to materials. Our tests of the effect of the inhibitors on the fuel consumption rate were performed with heptane and methanol fuels. For the more traditional extinction tests, we present some data with heptane and methanol as the fuel, but most were performed using methane. Tests with flames of methane are warranted since they have been shown to provide similar inhibitor rankings for extinction compared to other larger hydrocarbon fuels [17]. Also, although methane oxidation is atypical of that of larger hydrocarbons, Babushok and Tsang have recently observed [18] that for a wide variety of hydrocarbons (including methane) the burning velocity is most sensitive to the rates of the same reactions. Since these reactions are the ones most influenced by an inhibitor, the trends in inhibitor effectiveness are the same for most hydrocarbons.

EXPERIMENT

A cup burner [19, 20] was used for the tests. The cylindrical glass cup, 28 mm outer diameter was positioned with the top at a height of 20.5 cm inside a 53.3 cm tall, 9.5 cm inner diameter glass chimney. A 7.5 cm thick bed of glass beads (6 mm dia) at the base of the chimney provided uniform flow in the air stream. Fuels were methane, methanol, or heptane. For the methane tests, the fuel cup was filled with 3 mm dia.

glass beads, with two 15.8 mesh/cm stainless steel screens (separated by 1 mm) at the top. For the liquid fuels, a dual syringe-pump (Yale Apparatus* model YA-12) system provided fuel at measured rates. In the first tests, the fuel consumption rate of the burner was determined by adjusting the pumping rate such that the fuel was flush at the edge of the glass fuel cup. This approach, while apparently working well, required long wait periods (several minutes) between changes in the feed rate to insure that the fuel level remained at a constant level. A subsequent method used an overflow system as in ref. [20]. Gas flows were measured with digitally-controlled mass flow controllers (Sierra 860) with a quoted repeatability of 0.2 %, which have been calibrated with bubble (Gillian Gilibrator), piston (Bios 20K), and dry (American Meter Co. DTM-200A) flow meters so that their uncertainty is 2 % of indicated flow.

The organometallic inhibitors were added to the air stream using multi-stage saturators in controlled temperature baths. The $Fe(CO)_5$ was added at volume fractions up to 950 ppm using a two-stage saturator described previously [9]. The TMT was added using an identical two-stage saturator, with >50 cm^3 of TMT in each stage. The water bath was maintained at (0 ± 0.2) °C or (43.2 ± 1.0) °C with a maximum carrier gas flow 0.43 L/min or 0.81 L/min for low and high values of X_{in}, respectively. For the MMT, the saturator had three stages, each a 20 cm long, 2.36 cm inner diameter stainless steel tube, and the entire apparatus was submerged in a controlled temperature bath (Neslab). The bath temperature was typically (85 ± 0.2) °C except the highest concentration, which as at (92.5 ± 0.2) °C; the maximum flow of carrier gas for this saturator was 1.5 L/min. The mole fraction of the organometallic inhibitors in the air stream was calculated based on the measured air flow, measured carrier gas flow (N_2 or CO_2), and vapor pressure of the agent at the bath temperature, assuming saturated carrier gas. The parameters in the Antoine equation $\log_{10}(P)=A-B/(T+C)$ are (A,B,C): (6.77273, 4.0932, 7.2283), (1258.22, 1286.16, 1882), and (211.587, 235.846, 200) for $Fe(CO)_5$ [21], TMT [22], and MMT [23]. Since the vapor pressure of MMT is much lower than that of the other agents, it was necessary to preheat the burner and lines prior to addition of this agent. The air was preheated to >50 °C and served to convectively heat the burner to >(35.0 ± 0.5) °C before and during the tests to reduce the likelihood of MMT condensation.

For bromine as the inhibitor, all flow tubes downstream of agent addition as well as the burner base were replaced with ones made of Teflon to avoid reaction. A computer-controlled syringe pump (Yale Apparatus YA-12) and disposable syringe (10 cc BD 10cc22G1) added the liquid Br_2, via a stainless steel needle in a viton septum, to the tubing carrying the air and CO_2. A 2.1 m length of tubing prior to the burner was used

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* Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment are necessarily the best available for the intended use.

to insure agent mixing with the air, and complete Br_2 evaporation was observed to occur within a tubing length of less than 1 m.

To determine the extinction condition for pure CO_2, the CO_2 was added to the air flow in increasing volume (in increments of < 1 %) until lift-off was observed. The test was repeated at least three times. In the presence of a second inhibitor, that agent was first added to the air stream at a constant volume fraction, and then the amount of added CO_2 required for lift-off was determined as in the pure CO_2 case. The amount of CO_2 required for lift-off is reported as its volume fraction in the burner co-flow stream (i.e., the sum of the air, added CO_2, and carrier-gas CO_2). (Note that in some early tests, to be described in Table 1, N_2 was used as the carrier gas instead of CO_2. In those cases, we included the N_2 in the CO_2 flow by correcting for differences in specific heat between the two.) The fuel gas is methane (Matheson UHP, 99.9 %), and the oxidizer is house compressed air (filtered and dried) which is additionally cleaned by passing it through an 0.01 μm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The chemicals used were $Fe(CO)_5$ (Aldrich), TMT (Alfa Aesar), MMT (Alfa Aesar), CH_3OH (Aldrich, 99.8 %), Br_2 (Aldrich, 99.5 %), CF_3Br (Great Lakes), N_2 (boil-off), and CO_2 (Airgas).

The uncertainty analysis consists of calculation of individual uncertainty components and root mean square summation of components [24]. All uncertainties are reported as *expanded uncertainties*: $X \pm U$, where U is ku_c, and is determined from a combined standard uncertainty (estimated standard deviation) u_c, and a coverage factor $k = 2$ (level of confidence approximately 95 %). Likewise, when reported, the relative uncertainty is $U / X \cdot 100$ %, or $ku_c / X \cdot 100$ %. The expanded relative uncertainties for the experimentally determined quantities in this study are: CO_2 volume fraction, 4 %; inhibitor volume fraction for organometallics, CF_3Br, and Br_2: 5 %, 2.7 %, and 2.0 %; or otherwise as noted on the figures.

RESULTS AND DISCUSSION

We conducted our first tests in a heptane-fueled cup burner. In the absence of $Fe(CO)_5$, the extinction condition occurs at a CO_2 volume fraction of (19.2 ± 0.76) % (the value is somewhat low due to the low air volumetric flow of 25 l/min in these tests). With about 450 ppm of $Fe(CO)_5$ added to the air stream, the CO_2 volume fraction required for extinction is (18.3 ± 0.74) %, indicating a reduction of only about 5 %. This result is unexpected since adding 150 ppm of $Fe(CO)_5$ to a premixed methane-air flame reduces by a factor of eight the amount of CO_2 required to halve the burning velocity.

For a cup-burner flame, addition of $Fe(CO)_5$ or CO_2 might not only change the extinction condition, but might also change the heat release rate at each agent volume fraction. We measured the fuel consumption rate as an approximate measure of the heat release in the flame. Figure 1 shows the heptane consumption rate in a cup burner

as a function of the CO_2 mole fraction in the air stream. The upper curve shows the results for pure CO_2, while the lower curve presents the results for addition of 450 ppm of $Fe(CO)_5$ to the air stream prior to addition of CO_2 to the air stream. As the figure shows, the presence of $Fe(CO)_5$ causes a 16 % to 38 % reduction in the fuel consumption rate for CO_2 mole fractions up to 75 % of extinction.

Unfortunately, the results in Figure 1 are confounded by the sooting tendencies of heptane cup-burner flames. Heat transfer to the pool surface is enhanced by soot in the gas phase, as well as by soot on the hot chimney walls. With addition of $Fe(CO)_5$, soot production was visually observed to be reduced, which is consistent with its known effects on the sooting tendencies of flames (see ref. [4] and the references therein).
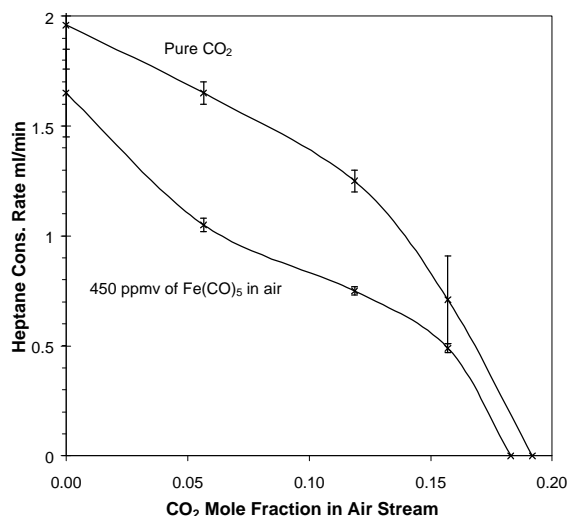

Figure 1 - **Heptane consumption rate in cup-burner flame as a function of added CO_2 mole fraction with and without 450 ppm $Fe(CO)_5$ added to the air stream.**

Figure 2 - **Methanol consumption rate in cup-burner flame as a function of added CO_2 mole fraction with and without 450 ppm $Fe(CO)_5$ added to the air stream.**
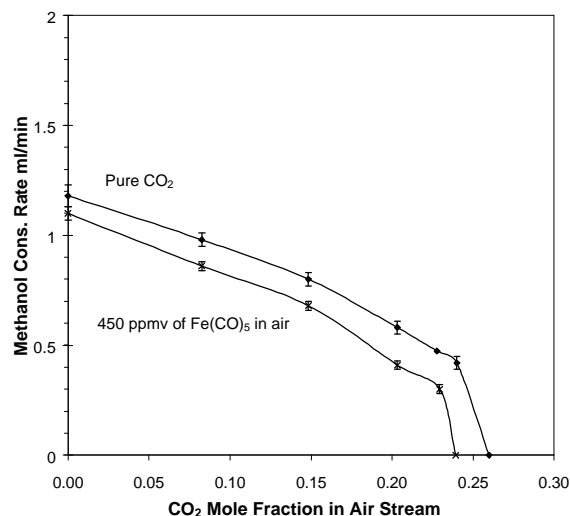
At higher mole fractions of added CO_2, soot formation is visually observed to be suppressed, with and without addition of $Fe(CO)_5$. We desire to eliminate the complicating effects of soot formation in cup-burner flames. In order to retain a liquid fuel but virtually eliminate sooting, we ran additional tests with methanol as the fuel. The methanol-air flames extinguished at a CO_2 mole fraction of (26.0 ± 1.1) % without $Fe(CO)_5$, and (23.9 ± 1.0) % with 450 ppm of $Fe(CO)_5$ added to the air stream. As with heptane, the reduction in the amount of CO_2 required for extinction from added $Fe(CO)_5$ is small, here only about 8 %. Figure 2 shows the change in the methanol consumption rate with addition of 450 ppm of $Fe(CO)_5$ to the air stream, as a function of the amount of added CO_2. We see that without the confounding effects of soot formation, the fuel consumption rate is reduced by a nearly constant amount. The fuel consumption rate is reduced somewhat, but the reduction is not nearly as high as might be expected based the overall reaction rate reduction in premixed methane-air flames.

To further understand the influence of iron in cup-burner flames, we also conducted tests with methane fuel. In these tests, $Fe(CO)_5$ could be added to either the fuel or the air stream, removing the uncertainty associated with agent transport to the relevant reaction zone. Table 1 summarizes the results for all of the tests. The top line shows that (15.7 ± 0.6) % CO_2 is required to extinguish this flame. The next two lines show that addition of $Fe(CO)_5$ to the air stream at quite high mole fractions (450 ppm and 924 ppm) causes only a (9.6 ± 0.5) % and (13.5 ± 0.8) % reduction in the amount of CO_2 required for extinction. If we add 1 % CH_4 to the air stream to change the flame location and hence the scalar dissipation rate, the reduction in the CO_2 required for extinction with addition of 450 ppm of $Fe(CO)_5$ is slightly greater, but still only about (10.7 ± 0.6) %. Likewise, addition of $Fe(CO)_5$ to the fuel stream at either 450 ppm or 4500 ppm causes only a (1.3 ± 0.1) % and (2.6 ± 0.2) % reduction in the amount of CO_2 required. These results are in contrast to those for CF_3Br with CO_2 in the cup burner which are shown at the bottom of the table. There, we see that addition of CF_3Br to either stream at mole fractions which would approximately halve the burning velocity leads to a reduction of the CO_2 required for extinction by a factor of two to three. Clearly, CF_3Br and $Fe(CO)_5$ behave quite differently in the cup burner with respect to their ability to reduce the CO_2 requirement for extinction.

Table 1 - **Extinction volume fraction of CO_2 in methane-air cup burner with and without various amounts of $Fe(CO)_5$ or CF_3Br added to the fuel or air stream (air flow =41.6 l/min).**

Catalytic Inhibitor			Vol % CO_2 at Extinction	% Reduction from Pure CO_2
None	-	-	15.7 ± 0.6	-
$Fe(CO)_5$	450 ppm	in Air	14.1 ± 0.6	9.6 ± 0.5
"	924 ppm		13.5 ± 0.5	13.5 ± 0.8
"	450 ppm	in Air w/ 1% CH_4	14.0 ± 0.6	10.7 ± 0.6
"	450 ppm	in Fuel	15.4 ± 0.6	1.3 ± 0.1
"	4500 ppm		15.2 ± 0.6	2.6 ± 0.2
CF_3Br	1.3 %	In Air	4.4 ± 0.2	72.0 ± 4.1
"	11 %	In Fuel	8.7 ± 0.3	44.2 ± 2.5

The question naturally arises as to whether this is specific to iron, or characteristic of super-effective inhibitors in general. To investigate this, we examined the cup-burner extinction data of TMP and DMMP from researchers at NMERI [25]. In their tests, they found that about 5 % of DMMP was required for extinction, or 5.3 % to 6.9 % for TMP. It is surprising that so much is required to extinguish cup-burner flames considering that in methane-air flames, these phosphorus compounds have been shown to be about

seventeen and three times more effective than CF_3Br in premixed [26] and diffusion flames [27], respectively.   In these tests in cup burners, DMMP and TMP are less effective on a volume basis than CF_3Br; on a mass basis, they are only about as effective as CO_2. Further, at these concentrations, the agent could be working through oxygen starvation. For example, for DMMP and TMP, the stoichiometric mole fraction in air is about 4.5 % and 5.0 %. Hence, the actual mole fractions required for extinguishment are close to those at which the agent would consume all of the available oxygen in the air stream.

The present discussion of the results in Table 1 may lead one to conclude that the super-effective agent $Fe(CO)_5$ is not effective for suppressing cup burner flames. If we conduct tests for a continuous range of concentrations for added $Fe(CO)_5$ and CF_3Br, however, a more comprehensive picture emerges. Below, we present additional detailed data for CO_2 extinction of methane cup-burner flames for TMT, MMT, Br_2, and CF_3Br.

Instead of finding the mole fraction of CO_2 required to extinguish a cup burner flame with a fixed, constant amount of catalytic agent, we can perform the tests for a range of catalytic inhibitor mole fraction in the air stream. Figure 3a shows the results of such tests for five catalytic agents, and Figure 3b shows the same data for the region corresponding to the dotted box in the upper left of Figure 3a.
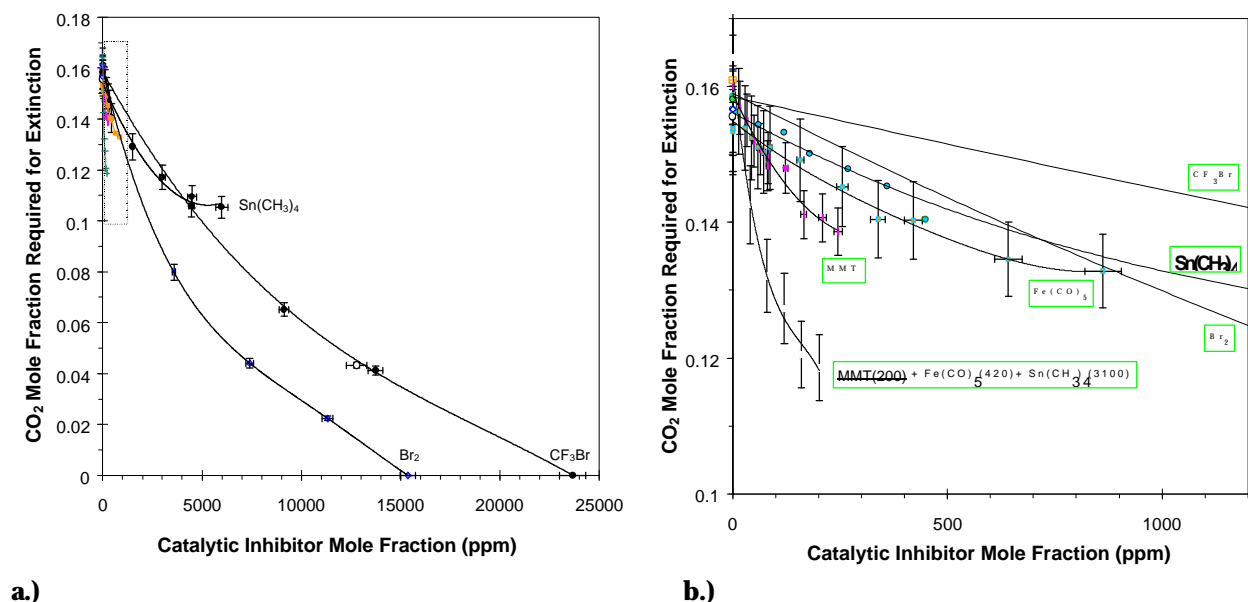

a.)   b.)

Figure 3 – Mole fraction of CO_2 required for methane-air cup-burner flame extinction as a function of catalytic inhibitor mole fraction, CF_3Br, Br_2, $Fe(CO)_5$, TMT, MMT, or a blend of the last three (b. has expanded x- and y-axes compared to a.).

For extinction of these methane-air flames, pure CO_2 is required in the air stream at mole fraction of (15.7 ± 0.6) %, whereas CF_3Br, a catalytic agent, is required at (2.4 ± 0.1) %. As

Figure 3a shows, adding CF_3Br at mole fractions below the extinction value greatly reduces the amount of CO_2 required for extinction. For example, adding half of the extinction value of CF_3Br reduces the amount of CO_2 required by 70 %. The curvature in the line for CF_3Br in Figure 3a indicates that, as described previously [14], the combination of CF_3Br and CO_2 is synergistic; that is, when combined, less of each is required for extinction than one would expect based on a linear interpolation of the results for each individually. The curve for Br_2 indicates that it is about twice as effective as CF_3Br, confirming the dominance of the Br molecule and the lesser but apparent role of the CF_3 radical (as has been shown for premixed flames [28]).

In the sequence CF_3Br, TMT, $Fe(CO)_5$, and MMT, each is about twice as effective as its predecessor at low mole fraction, so that $Fe(CO)_5$ is about four times as effective as CF_3Br. While this performance is noteworthy, it is far less than was observed in premixed flames, for which the benefit was one to two orders of magnitude for $Fe(CO)_5$ as compared to CF_3Br. Interestingly, TMT, $Fe(CO)_5$, and MMT all have a decreasing slope as their mole fraction increases. This is similar to their behavior in premixed and diffusion flames, leading one to believe that cause of the loss of effectiveness is the same (condensation of active species).

In previous work it has been argued that to obtain the good performance by the super-effective agents, it might be possible to add small, non-condensing amounts of catalytic agents together with an inert agent. We tested this claim by adding a blend of the three catalytic metals to the air/CO_2 stream. In the bottom curve of Figure 3b., MMT, $Fe(CO)_5$, and TMT are added in linearly increasing amounts, up to 200 ppm, 420 ppm, and 3100 ppm, respectively, and the amount of CO_2 for flame extinction is plotted as a function of the MMT mole fraction. As shown, the agents do work together to reduce the amount of CO_2 required for extinction, and (within the uncertainty of the measurements) the blend does not lose its effectiveness. Nonetheless, the performance of the blend is only about half what would be expected from sum of the individual contribution from each component. Unfortunately, even with these relatively high mole fractions of the inhibitors, we reduce the amount of CO_2 required by only 25 %.

On a molar basis, the organometallic compounds *are* effective at reducing the amount of CO_2 required for cup burner extinction as compared to CF_3Br; however, their relative performance is much poorer than one would expect based on their behavior in premixed flames. Two possible causes of the loss of inhibition effectiveness are the same as were discussed previously for premixed and counterflow diffusion flames, namely 1.) saturation of the catalytic cycles and 2.) condensation of active gas-phase species. They are discussed below.

The saturation of the catalytic cycles is deemed to be unlikely. This is based on two results shown in Figure 3: those for Br_2, and those for the blend of MMT, $Fe(CO)_5$, and TMT. If the loss of effectiveness of each of the organometallic agents was due to depletion of the radical pool, the region of the flattening behavior in the curve of each

would occur near the same value of X_{CO_2}. The experiments with Br_2 were designed to test this. Since Br_2 does not have a fuel effect (i.e. inhibition due to oxygen depletion) as does CF_3Br, it can more clearly test the role of radical recombination. As Figure 3b shows, the data for Br_2 is very linear in the region where the other curves are starting to flatten out, implying radical saturation is not the cause of the loss of effectiveness of the metals. The possibility of radical depletion is further explored in tests with a combination of MMT, $Fe(CO)_5$, and TMT. If the agents added alone were losing their effectiveness due to radical depletion, adding a second (or third) catalytic agent to the mix would not provide additional inhibition. In the bottom curve of Figure 3b, however, the blend of all three agents (added up to (200, 420, and 3100) ppm each, in linearly increasing amounts, and plotted as a function of the MMT mole fraction) clearly shows additional inhibition over MMT alone, providing evidence against radical saturation.

We speculate that particle formation is the cause of the degraded performance of the metal agents. The approximate agent mole fraction for the loss of effectiveness is an order of magnitude higher for TMT (4000 ppm) than for the iron or manganese (400 ppm) (as occurs in premixed flames) [5], which is consistent with the higher vapor pressure for the tin compounds. A visible outer annulus, apparently particles, was observed in all flames with added metals, and the blackbody radiation from that region increased with higher agent mole fraction. Finally, as discussed in refs. [10, 29], the particle formation rates appear to be linked to their residence time in the cooler regions of the flame. Since the present cup-burner flames have quite different flow fields than either premixed or counterflow diffusion flames, it is likely that the condensation behavior in them is different. It is possible that metal compounds added to the air stream are sequestered as particles which are then convected away from the relevant radical recombination zones of the flame before they can affect the flame chemistry.

CONCLUSIONS

We have presented the first data on the extinction characteristics of highly effective catalytic agents added to a cup burner flame together with CO_2. The order of increasing performance is: CF_3Br, TMT, $Fe(CO)_5$, and MMT, with each about twice as effective at low mole fraction as its predecessor. The data indicate that while these compounds are very effective compared to CF_3Br on a molar basis, their relative performance benefit over that agent is far less than in premixed flames. Further, they experience a loss in effectiveness at reducing the amount of CO_2 required for extinction, which is reminiscent of the behavior in premixed flames. We postulate (but have not demonstrated) that the loss in effectiveness is due to condensation of the metal, metal oxides, or metal hydroxides. For methanol, the effect of the metal compounds on the fuel consumption rate (caused by the heat feedback to the liquid fuel surface) is small. For heptane, the effect is somewhat larger, and this is postulated to be due to reduced soot formation. Finally, while we have shown that combinations of organometallic catalytic agents can reduce the amount of CO_2 required for extinction, addition of 200 ppm of MMT, 420

ppm of $Fe(CO)_5$, and 3100 ppm of TMT reduced the amount of CO_2 required for extinction by only 25 %. This reduction is about half that which would have been expected based on a linear combination of the effect from the individual components. In future research, it is suggested to determine if phosphorus compounds, which have also been shown to be effective in premixed and counterflow diffusion flames, are effective at reducing the amount of CO_2 required to extinguish a cup burner flame. It has been postulated that the reason for the lower effectiveness in these diffusion flames is particle formation and the subsequent sequestering of the active gas-phase inhibiting compounds prior to their introduction to the stabilization regions of the flame. It would be helpful to perform measurements of particles in these flames via traditional laser scattering and extinction to determine if this is indeed the reason for loss of effectiveness.

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